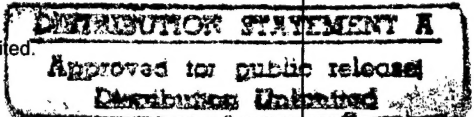
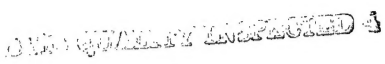


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6. AUTHOR(S) Prof J.M.Dyke				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry University of Southampton Southampton SO9 5NH, England			8. PERFORMING ORGANIZATION REPORT NUMBER SPC-91-4004	
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13. ABSTRACT (Maximum 200 words) The contractor has characterized some chemionization reactions of Group II metals with atmospheric oxidants using electron spectroscopy and mass spectrometry. The contractor has measured the valence ionization energies of LiO, NaO and KO produced from the reactions of appropriate Group I metals with N ₂ O and O ₃ . 				
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Final Report

on

Contract No. F6170891W0807

Contract Period 1.8.91.-31.7.92.

Principal Investigator: Prof. J.M. Dyke
Dept. of Chemistry
The University
Southampton SO9 5NH
U.K.

Title: *Photoelectron and Chemielectron Spectroscopy
of Metal Oxides of Atmospheric Importance*

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Products of the gas-phase reactions $M + N_2O$ and $M + O_3$, where $M=Na$ or K , have been investigated with u.v. photoelectron spectroscopy and the observed bands have been assigned with the assistance of results from *ab initio* molecular orbital calculations.

For the $M + N_2O$ reactions, the observed products were $MO + N_2$. Measurement of the photoelectron bands associated with the metal monoxide, MO , allowed determination of the first adiabatic ionization energies (AIEs) of NaO and KO . The values obtained were $AIE [NaO(X^2\Pi)] = (7.1 \pm 0.1) \text{ eV}$ and $AIE [KO(X^2\Pi)] = (6.9 \pm 0.1) \text{ eV}$. A similar study of the $Li + N_2O$ reaction gave $AIE [LiO(X^2\Pi)] = (7.6 \pm 0.2) \text{ eV}$.

The reactions $M + O_3$ with $M = Na$ or K , were observed to give $MO + O_2$ as the major reaction products. However, for each reaction a band was observed which was assigned to the first ionization energy of the secondary reaction product, MO_2 . From the spectra obtained, the first adiabatic ionization energies of NaO_2 and KO_2 were measured as

$$AIE [NaO_2(X^2A_2)] = (6.2 \pm 0.2) \text{ eV and}$$

$$AIE [KO_2(X^2A_2)] = (5.7 \pm 0.1) \text{ eV.}$$

For both the $M + N_2O$ and $M + O_3$ reactions, production of $MO A^2\Sigma^+$ was found to be favoured relative to production of the $MO X^2\Pi$ state, a result which has important implications in understanding the sodium night-glow in the mesosphere.

The ionization energy values determined in this work allow determination of ground state ionic dissociation energies. For example, for NaO^+ and KO^+ in their ground states, D_0 has been derived as (0.60 ± 0.31) and $(0.15 \pm 0.14) \text{ eV}$ respectively.

Reaction enthalpies can also be derived from the thermodynamic values derived in this work, for ion-molecule reactions of the type



For example for $M = Na$, ΔH_1 and ΔH_2 can be derived as $-(4.98 \pm 0.11)$ and $(0.23 \pm 0.44) \text{ eV}$ respectively.

Work performed under this part of the contract, involving the study of Group I metals with oxidants, has been written up for publication and will soon be submitted to Journal of Chemical Physics. A preprint of this work is enclosed.

As part of an on-going experimental programme in chemiionization using chemielectron and chemiion spectroscopy, the ionization chamber of an electron spectrometer has been modified to allow ions and electrons to be sampled from the same reaction cell under a given set of experimental conditions simply by choosing the sign and magnitude of the extraction voltage on the cell. This experimental arrangement has been used to study the reaction of the group II metals (calcium, strontium and barium) with the oxidants $O_2(X^3\Sigma_g^-)$, $O_2(a^1\Delta_g)$ and $O(^3P)$. The results have been interpreted in terms of a simple thermodynamic model that is consistent with these reactions proceeding via long lived collision intermediates. The electron energy distributions have been interpreted in terms of a simple potential energy model, and the possibility

of the inclusion of an associative ionization reaction into a kinetic model of metal chemistry in the upper atmosphere has been considered. This work will soon be written up for publication.

Taking the $\text{Ba} + \text{O}_2(\text{X}^3\Sigma_g^-)$, $\text{Ba} + \text{O}_2(\text{a}^1\Delta_g)$ and $\text{Ba} + \text{O}(\text{}^3\text{P})$ reactions as examples, the electron energy distributions and ions seen in the $\text{Ba} + \text{O}_2(\text{X}^3\Sigma_g^-)$ case can be interpreted in terms of the following processes:



Adding $\text{O}_2(\text{a}^1\Delta_g)$ to the $\text{Ba} + \text{O}_2(\text{X}^3\Sigma_g^-)$ reaction mixture reduces the ion and electron yield by removing Ba atoms via the neutral reaction



Chemiionization can, however, occur via



On adding $\text{O}(\text{}^3\text{P})$ to the system, BaO is produced via



which then undergoes chemiionization via reaction (5)

The new apparatus proved very useful in distinguishing between primary and secondary ions via the saturation current method, and in associating a given primary ion to an observed chemielectron band. The high kinetic energy offsets of the experimental chemielectron bands were used to estimate the exothermicities of the observed chemiionization reactions. Negative ion formation, a competing process to electron production in chemiionization, has also been investigated for the Group II metal plus oxidant reactions and in each case negative ion production has been found to be a minor channel.

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4. TITLE AND SUBTITLE PHOTOELECTRON AND CHEMIELECTRON SPECTROSCOPY OF METAL OXIDES OF ATMOSPHERIC IMPORTANCE				5. FUNDING NUMBERS F6170891W0807	
6. AUTHOR(S) PROFESSOR J.M. DYKE					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Southampton Department of Chemistry Highfield Southampton SO9 5NH, UK				8. PERFORMING ORGANIZATION REPORT NUMBER	
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REPORT OF INVENTIONS AND SUBCONTRACTS

(Pursuant to "Patent Rights" Contract Clause) (See Instructions on Reverse Side.)

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1a. NAME OF CONTRACTOR/SUBCONTRACTOR J.M. DYKE		c. CONTRACT NUMBER F0170891W0807		2a. NAME OF GOVERNMENT PRIME CONTRACTOR		c. CONTRACT NUMBER		3. TYPE OF REPORT (X one) a. INTERIM <input checked="" type="checkbox"/> b. FINAL	
b. ADDRESS (Include ZIP Code) THE UNIVERSITY SOUTHAMPTON, SO9 5NH, UK		d. AWARD DATE (YYMMDD)		b. ADDRESS (Include ZIP Code)		d. AWARD DATE (YYMMDD)		4. REPORTING PERIOD (YYMMDD) a. FROM 91.08.01 b. TO 92.07.31	

SECTION I - SUBJECT INVENTIONS

5. "SUBJECT INVENTIONS" REQUIRED TO BE REPORTED BY CONTRACTOR/SUBCONTRACTOR (If "None," so state)

a. NAME(S) OF INVENTOR(S) (Last, First, MI)	b. TITLE OF INVENTION(S)	c. DISCLOSURE NO., PATENT APPLICATION SERIAL NO. OR PATENT NO.	d. ELECTION TO FILE PATENT APPLICATIONS				e. CONFIRMATORY INSTRUMENT OR ASSIGNMENT FORWARDED TO CONTRACTING OFFICER
			(1) United States (a) Yes (b) No	(2) Foreign (a) Yes (b) No	(1) Yes (2) No	(1) Yes (2) No	
NONE	NONE						

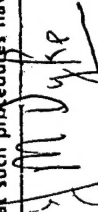
SECTION II - SUBCONTRACTS (Containing a "Patent Rights" clause)

6. SUBCONTRACTS AWARDED BY CONTRACTOR/SUBCONTRACTOR (If "None," so state)

a. NAME OF SUBCONTRACTOR(S)	b. ADDRESS (Include ZIP Code)	c. SUBCONTRACT NO.(S)	d. IF AN "PATENT RIGHTS"		e. DESCRIPTION OF WORK TO BE PERFORMED UNDER SUBCONTRACT(S)	f. SUBCONTRACT DATES (YYMMDD)	
			(1) Clause Number	(2) Date (YYMM)		(1) Award	(2) Estimated Completion

SECTION III - CERTIFICATION

7. CERTIFICATION OF REPORT BY CONTRACTOR/SUBCONTRACTOR (Not required if Small business or Non-Profit organization) (X appropriate box)

a. I certify that the reporting party has procedures for prompt identification and timely disclosure of "Subject Inventions," that such procedures have been followed and that all "Subject Inventions" have been reported.	
b. NAME OF AUTHORIZED CONTRACTOR/SUBCONTRACTOR OFFICIAL (Last, First, MI) J.M. DYKE	d. SIGNATURE 
b. TITLE PROFESSOR	e. DATE SIGNED 92.07.14

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